

CHROM. 16,195

## DETERMINATION OF TOTAL OXYGENATES IN FISCHER-TROPSCH LIQUID PRODUCTS

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(First received July 13th, 1983; revised manuscript received August 4th, 1983)

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### SUMMARY

Gas and liquid chromatographic techniques for a detailed determination of total oxygenates (alcohols, ketones, esters and acids) in Fischer-Tropsch aqueous and hydrocarbon condensed phase products are presented. Aqueous oxygenates ( $C_1-C_8$ ) are determined by direct, split injection onto a bonded-phase fused-silica capillary column and by ion chromatography. Oxygenates ( $C_6-C_{40}$ ) in the hydrocarbon phase are isolated by low pressure liquid chromatography followed by on-column fused-silica gas chromatographic analyses. A rapid isolation of  $C_2^+$  oxygenates in the hydrocarbon phase by Sep-Pak<sup>R</sup> silica cartridge is also described. The techniques have proven useful in monitoring a large scale Fischer-Tropsch pilot unit.

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### INTRODUCTION

The condensed liquid products ( $C_5^+$  hydrocarbon + aqueous phases) from the Fischer-Tropsch (F-T) synthesis gas ( $CO + H_2$ ) process may contain a relatively large amount of oxygenates. These oxygenates are normally of various functional groups (alcohols, ketones, esters, carboxylic acids, aldehydes) and may be present over a wide carbon number range, e.g.  $C_1-C_{40}$ .

Synthesis gas has been successfully converted to high octane gasoline by a combination of F-T synthesis followed by product upgrading with a ZSM-5 class catalyst. To study the effects of process variables on the composition of the F-T products analytical methods have been developed for a detailed determination of total oxygenates in the condensed products. Published F-T analytical methods<sup>1-8</sup> have dealt mainly with relatively low molecular weight components produced during F-T catalyst studies with little emphasis on the higher boiling oxygenates which may be produced in large scale reactors. Other workers<sup>9</sup> have resolved some of the major oxygenates in the hydrocarbon and aqueous phases; however, hydrocarbon interference prevented the determination of all other oxygenates present and thus quantitation of total oxygenates could not be obtained.

In this paper, analytical techniques for the determination of high boiling oxygenates in the hydrocarbon phase previously published by Di Sanzo<sup>10</sup> have been

expanded to include the determination of low boiling oxygenates in both the hydrocarbon and aqueous phases by employing state-of-the-art fused-silica capillary columns and on-column injection. Finally, an alternative rapid method for the isolation of  $C_2$ – $C_{25}^+$  oxygenates in the hydrocarbon phase is described.

## EXPERIMENTAL

### *Gas chromatography/gas chromatography–mass spectrometry (GC/GC–MS)*

All GC analyses were performed either on a Hewlett-Packard (H-P) 5880 gas chromatograph equipped with an (H-P) cool on-column capillary injector or a Varian 6000 gas chromatograph equipped with a capillary inlet and a J&W Scientific (Rancho Cordova, CA, U.S.A.) on-column injector. Bonded phase fused-silica capillary columns were purchased from J&W Scientific. Qualitative analysis was performed on a Hewlett-Packard 5985B GC-MS-DS system employing fused-silica capillary columns.

### *Acidic oxygenates*

A Dionex Model 10 ion chromatograph was employed (Dionex, Sunnyvale, Ca, U.S.A.) under the following conditions: Columns: normal ICE anion separator, ICE anion suppressor (Dionex); eluent: 0.0001 *M* hydrochloric acid, in deionized water; flow-rate: 0.8 ml/min; mode: linear; sensitivity: 3  $\mu$ mho; injection loop: 100  $\mu$ l.

A 10.00-ml aliquot of the aqueous sample was placed into a centrifuge tube and excess sodium hydroxide (0.1 ml 50% sodium hydroxide) was added to convert the volatile organic acids to their non-volatile sodium salts. The samples were evaporated to dryness on a steam bath under a stream of nitrogen. The salt residue was dissolved in 5.00 ml 1 *M* hydrochloric acid and diluted to the initial sample volume with deionized water. Spiking experiments with  $C_1$ – $C_3$  acids indicated that complete recovery of the acids is attained.

Sample solutions were diluted with deionized water as necessary to bring the acid peaks on scale and were analyzed by the method of standard additions.

$C_1$ – $C_3$  acids in the organic phases were pre-extracted with distilled water and analyzed by the above method.

### *Preparative liquid chromatography (LC)*

A previously published silica gel LC method<sup>10</sup> was followed for the isolation of  $C_6$ – $C_{40}$  oxygenates in the hydrocarbon (paraffins + olefins) phase. To minimize evaporation losses of the lower boiling oxygenates, *e.g.*  $C_6$ – $C_{10}$ , most of the solvents were removed with a Kuderna-Danish apparatus. Fractions were then transferred to modified nitrogen purged pre-weighed beakers and carefully taken to a constant weight.

### *Silica Sep-Pak procedure*

An alternative rapid method for the isolation of  $C_2$ – $C_{25}^+$  oxygenates was also developed.

Approximately 0.2 gram of the Fischer-Tropsch hydrocarbon phase is weighed into a micro silica-gel Sep-Pak (Waters Assoc., Milford, MA, U.S.A.) cartridge. The

cartridge is initially eluted with 5 ml of hexane to remove all of the olefins/paraffins and then with 2 ml of 10% methanol in methylene chloride to remove the  $C_2$ - $C_{25}$  oxygenates. Oxygenate carbon number distribution is then obtained by gas chromatography as described above. The activity of the Sep-Pak silica gel is critical for the retention of ketones and esters during the hydrocarbon elution. As an alternative to the Sep-Pak cartridge 20-44  $\mu\text{m}$  Biosil A silica gel (BioRad, Richmond, CA, U.S.A.) activated at 150°C for 12 h may be packed into a Pasteur pipette and then following the above elution procedure.

## RESULTS AND DISCUSSION

Fig. 1 represents a general scheme developed for total wt.-% oxygenate analysis in F-T liquid products. F-T condensed products normally consist of aqueous and hydrocarbon phases. Generally, the aqueous phase contains oxygenates up to only  $C_8$  due to solubility limitations whereas the hydrocarbon phase may consist of paraffins, olefins and smaller amounts of  $C_1$ - $C_{25}^+$  oxygenates. Under certain process conditions oxygenates up to  $C_{40}$  have been detected by the proposed methods.

### *Aqueous phase oxygenates*

Oxygenates in the aqueous phase are determined by direct aqueous injection onto a bonded-phase fused-silica capillary column employing a capillary splitter (Fig. 2). Most of the oxygenates (Table I) were identified by GC-MS and/or by spiking with authentic standards. Under optimum resolution for most of the oxygenates, the carboxylic acids (acetic, propanoic and butyric) exhibited broad peaks. Sharp acid

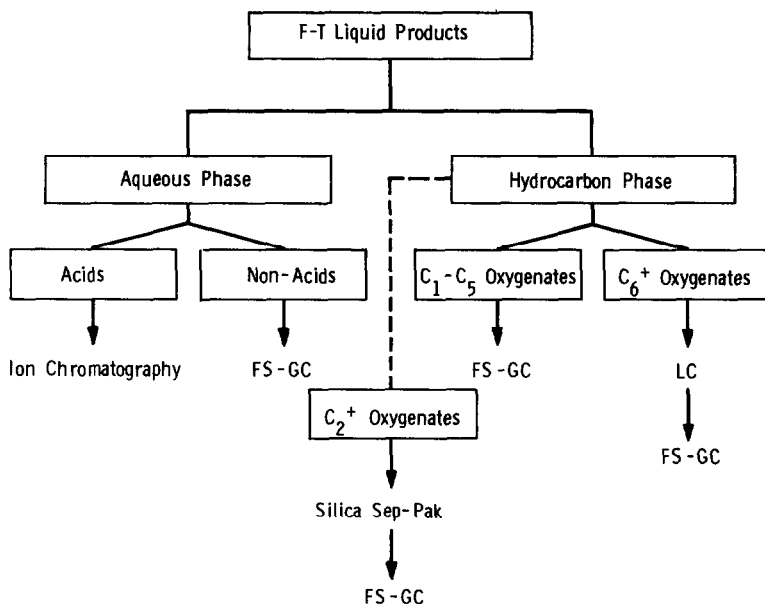


Fig. 1. Analytical scheme for the determination of total F-T oxygenates. FS-GC = fused-silica capillary gas chromatography.

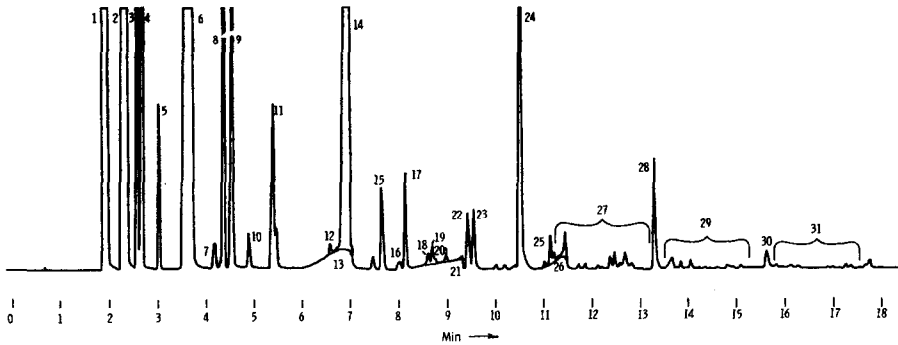


Fig. 2. Gas chromatogram of aqueous phase F-T oxygenates. Column: 30 m  $\times$  0.32 mm I.D. DB-5 (film thickness,  $df = 1.0 \mu\text{m}$ ); temperature: 35°C (6 min) 10°C/min to 150°C (2 min); injection: split 100:1; carrier gas: helium, 20 cm/sec; injector temp. = 270°C; detector temp. = 320°C. Peak identity, see Table I.

TABLE I

IDENTITIES OF MAJOR AQUEOUS PHASE OXYGENATES IN FIGS. 2 AND 3

Peak No.	Oxygenate
1	Methanol
2	Ethanol
3	2-Propanone
4	2-Propanol
5	2-Methyl-2-propanol
6	1-Propanol
7	<i>n</i> -Butanal
8	2-Butanone
9	2-Butanol
10	Ethyl acetate
11	2-Methyl-1-propanol
12	2-Methyl-2-butanone
13	Acetic acid
14	1-Butanol
15	2-Pentanone
16	<i>n</i> -Pentanal + 3-pentanone
17	2-Pentanol
18	Ethyl propanoate
19	Propyl acetate
20	Methyl butanoate
21	Propanoic acid
22	3-Methyl-2-butanol
23	2-Methyl-1-butanol
24	1-Pentanol
25	2-Hexanone
26	Butyric acid
27	Other C <sub>6</sub> oxygenates
28	1-Hexanol
29	Other C <sub>7</sub> oxygenates
30	1-Heptanol
31	Other C <sub>8</sub> oxygenates

peaks were observed only at relatively high GC column temperatures ( $> 100^{\circ}\text{C}$ ) at which temperature resolution for the other oxygenates could not be obtained. For quantitation, the aqueous phase was treated with solid  $\text{NaHCO}_3$  to a  $\text{pH} > 7$  prior to injection which chromatographically removed the acids and produced a stable baseline for accurate quantitation of the non-acidic oxygenates (Fig. 3). Response factors relative to the internal standard (2-methyl-2-butanol) were obtained in the expected oxygenates concentration range with pure components dissolved in water. Response factors for  $\text{C}_5$ – $\text{C}_8$  oxygenates which exhibited limited aqueous solubility were obtained on a neat basis. Generally, response factors agreed very well with those calculated from literature values<sup>11</sup> and were linear over the concentration range of interest. The acids were quantitated by ion chromatography.

### Hydrocarbon phase

*$\text{C}_1$ – $\text{C}_5$  oxygenates.* To prevent excessive evaporation losses, the  $\text{C}_5$ - oxygenates in the hydrocarbon phase were determined by three 1:1 (1 g sample + 1 g water) aqueous extractions and quantitated similarly to the aqueous phase analysis described above. Aqueous extraction recovery studies on  $\text{C}_1$ – $\text{C}_5$  oxygenates spiked into an oxygenate-free F-T hydrocarbon phase which was prepared as previously reported<sup>10</sup>, indicated that three aqueous extractions were sufficient to recover most of the major  $\text{C}_1$ – $\text{C}_5$  oxygenates (Table II). Oxygenate concentrations were corrected for extraction efficiency.

*$\text{C}_6$ – $\text{C}_{25+}$  oxygenates.* Weight percent analysis on the higher boiling oxygenates in the hydrocarbon phase were determined by preparative LC as previously described by Di Sanzo<sup>10</sup>. By the latter procedure, normally two separate LC fractions may be obtained for the oxygenates: one containing ketones, esters and trace aldehydes, the other containing alcohols and small amounts of carboxylic acids. Oxygenate carbon number distribution on each (or combined) LC fraction(s) was obtained by GC em-

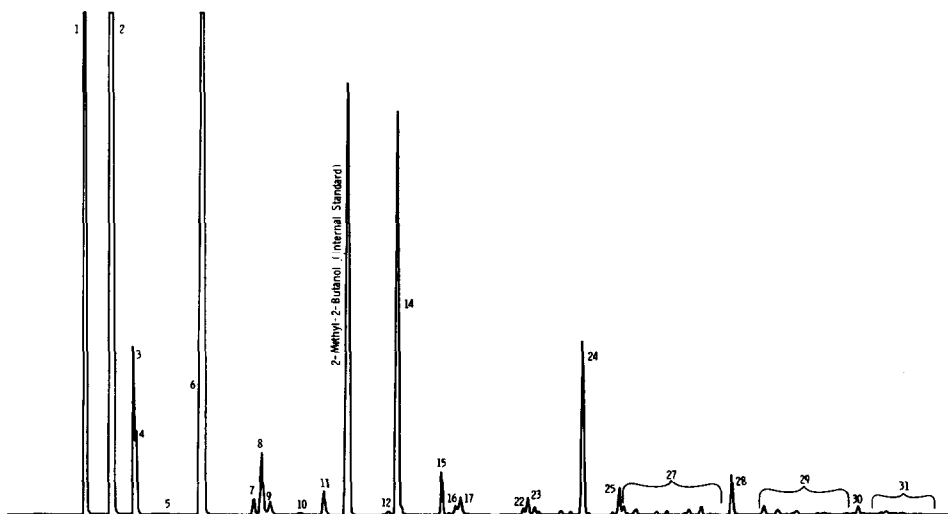


Fig. 3. Gas chromatogram of a F-T aqueous phase sample (acids removed) with internal standard. GC conditions: see Fig. 2.

TABLE II

EXTRACTION EFFICIENCIES OF C<sub>1</sub>-C<sub>5</sub> F-T OXYGENATES IN HYDROCARBON PHASE

Compound	% Recovery*
<i>Major</i>	
Methanol	101
Ethanol	99
1-Propanol	98
1-Butanol	96
1-Pentanol	79
<i>Minor</i>	
2-Propanone + 2-propanol	95
2-Methyl-2-propanol	93
2-Butanone	87
2-Butanol	94
2-Pentanone	55
2-Pentanol	87
2-Methyl-1-butanol	80

\* Three 1:1 aqueous extractions.

ploying cool on-column injections onto bonded-phase fused-silica capillary columns (Figs 4 and 5). Oxygenates up to C<sub>40</sub> have been detected by this method.

Table III represents a typical analysis obtained by the proposed methods. For simplicity the C<sub>6</sub><sup>+</sup> oxygenates are lumped.

#### Isolation of C<sub>2</sub><sup>+</sup> oxygenates by Sep-Pak silica gel cartridge

The slowest step in the above analytical scheme is the determination of the C<sub>6</sub><sup>+</sup> oxygenates which requires preparative LC for their isolation. A more rapid analytical approach was investigated involving silica gel Sep-Pak cartridges. This

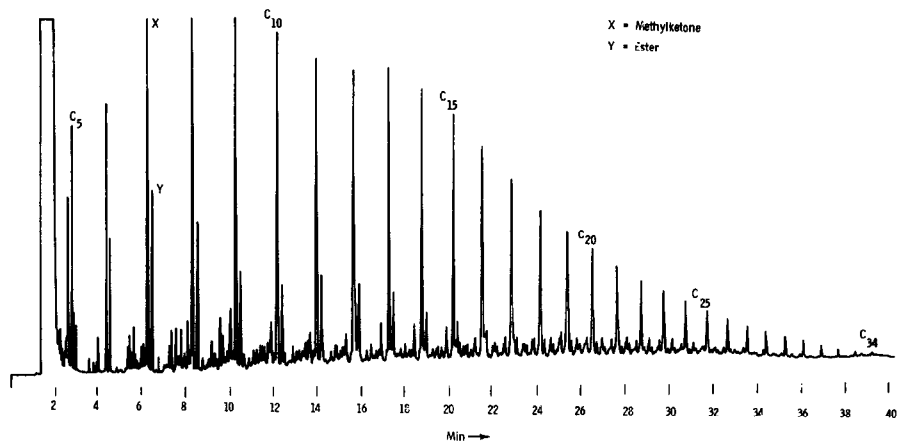


Fig. 4. Gas chromatogram of C<sub>5</sub><sup>+</sup> F-T organic phase ketones and esters isolated by LC (ref. 11). GC conditions: column, 15 m × 0.32 mm (d<sub>f</sub> = 0.25 μm) DB-5; temperature, 26°C, 6°C/min to 300°C; cool on-column injection.

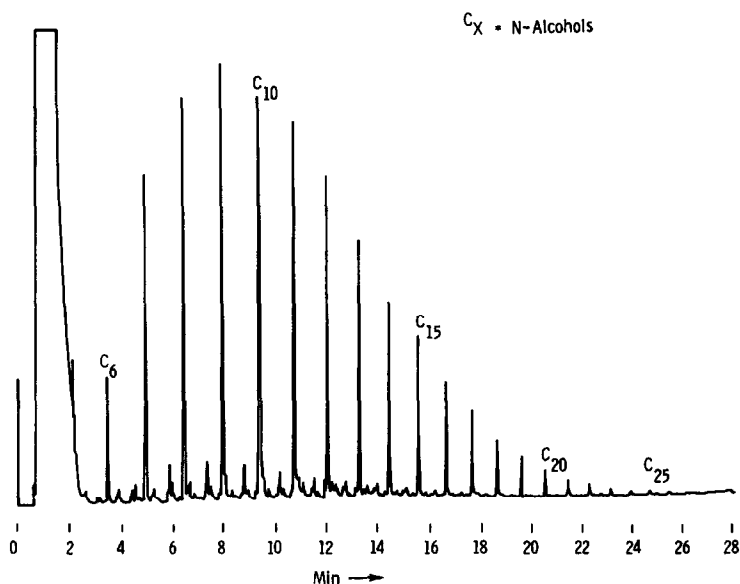


Fig. 5. Gas chromatogram of  $C_6+$  F-T organic phase alcohols and acids isolated by LC (ref. 11). GC conditions: see Fig. 4.

method is very similar to the LC isolation of the  $C_6-C_{25}+$  oxygenates except that it is carried out at the micro-scale level. Total oxygenate carbon number distribution is then obtained by GC as indicated in Fig. 6. This rapid and simple method may be employed as a qualitative daily monitoring of the oxygenate content of the F-T unit. Selected material balances may then be analyzed by the expanded scheme (Fig. 1) for a more accurate quantitation.

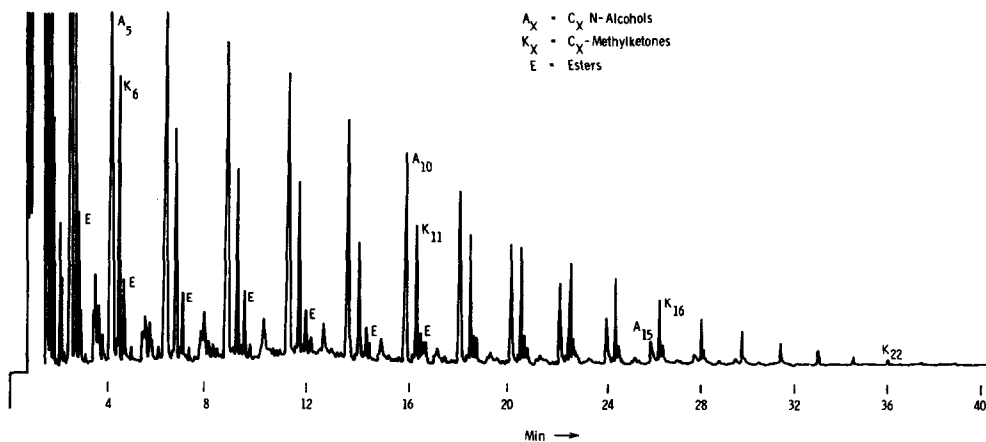


Fig. 6. Gas chromatogram of  $C_2+$  F-T oxygenates isolated from organic phase by the silica gel Sep-Pak method. GC conditions, see Fig. 4 except temperature increase,  $4^\circ\text{C}/\text{min}$ ; solvent, methanol-methylene chloride (10:90).

TABLE III  
OXYGENATES CONTENT OF F-T CONDENSED PHASE PRODUCTS

	<i>Aqueous phase</i>	<i>Hydrocarbon phase</i>	<i>Total</i>
<i>Non-acidic (wt.-%)*</i>			
Methanol	0.60	0.26	0.86
Ethanol	2.15	1.33	3.48
2-Propanone + 2-propanol	0.13	0.13	0.26
1-Propanol	0.61	1.03	1.64
<i>n</i> -Butanol	0.01	0.02	0.03
2-Butanone	0.04	0.11	0.15
2-Butanol	0.01	0.02	0.03
Ethyl acetate	0.0	0.0	0.0
2-Methyl-1-propanol	0.01	0.04	0.05
3-Methyl-2-butanone	<0.01	0.0	<0.01
1-Butanol	0.24	1.02	1.26
2-Pentanone	0.02	0.12	0.14
3-Pentanone + <i>n</i> -pentanal	<0.01	0.0	<0.01
2-Pentanol	0.01	0.04	0.05
3-Methyl-2-butanol	0.01	0.04	0.05
2-Methyl-1-butanol	<0.01	0.02	0.02
1-Pentanol	0.08	0.69	0.77
2-Hexanone	0.01		
1-Hexanol	0.01		
1-Heptanol	<0.01		
Other	0.04		
C <sub>6</sub> <sup>+</sup> Oxygenates (hydrocarbon phase)		6.76	6.76
<i>Acidic (ppm)*</i>			
Formic acid	<4	26	<30
Acetic acid	500	630	1130
Propanoic acid	100	430	530
<i>Total oxygenates (wt.-%)*</i>	4.07	11.71	15.78

\* Based on wt. aqueous phase + wt. hydrocarbon phase.

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